PB87-133104

Catalytic Dehydrohalogenation A Chemical Destruction Method for Halogenated Organics

Radian Corp., Research Triangle Park, NC

Prepared for

Environmental Protection Agency, Cincinnati, OH

Dec 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-133104

EPA/600/2-86/113
December 1986

CATALYTIC DEHYDROHALOGENATION: A CHEMICAL DESTRUCTION METHOD FOR HALOGENATED ORGANICS

by

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EPA Contract 68-02-3994

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U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-86/113	2.
3. RECIPIENT'S ACCESSION NO. PB87 133104/AS	
4. TITLE AND SUBTITLE CATALYTIC DEHYDROHALOGENATION: A CHEMICAL DESTRUCTION METHOD FOR HALOGENATED ORGANICS	5. REPORT DATE December 1986
	6. PERFORMING ORGANIZATION CODE Radian Corp.
7. AUTHOR(S) John M. Harden and George G. Ramsey	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation P. O. Box 13000 Research Triangle Park, NC 27709	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Hazardous Waste Engineering Research Laboratory Office of Research and Development U. S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE EPA/600/12
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

Dehydrohalogenation shows potential as a means for converting certain halogenated organics in wastes to inorganic salts and gaseous aliphatic compounds.

Dehydrohalogenation is a dehalogenation/elemination reaction that is initiated by a strong base. The resulting products are the halide salt, water, and an elimination compound.

A novel reagent, sodium or potassium hydroxide mixed with a polyethylene glycol, is a very effective dehydrohalogenation agent. This reagent is shown to dehalogenate six organic compounds that are representative of low molecular weight compounds encountered in hazardous wastes: CCl_4, $CHCl_3$, CH_2Cl_2, $C_2H_4Br_2$, and CCl_3NO_2. Kinetics data for the reactions of this reagent with the six compounds is given to allow reactor design and calculation of destruction efficiency.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO THE PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 46
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract Number 68-02-3994 to Radian Corporation. It has been subject to the Agency's peer and administrative review, and is approved for publication.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of state and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes an experimental program initiated in the Hazardous Waste Engineering Research Laboratory to validate the treatment of halogenated waste compounds by means of a novel dehydrohalogenated reagent. This reagent, composed of caustic mixed with a relatively small quantity of polyethylene glycol, has been shown to be effective in rapid yet controlled dehydrohalogenation in organic syntheses. The polyethylene glycol acts as a catalyst in the reaction. In this program, the reagent mixture chosen for experimentation was potassium hydroxide (KOH) and tetraethylene glycol (TEG). This reagent is referred to as KTEG. A total of seven compounds were tested in the dehydrohalogenation system. This document is intended for those concerned with chemical destruction of these seven halogenated solvents/pesticides.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

Dehydrohalogenation shows potential as a means for converting certain halogenated organics in wastes to inorganic salts and gaseous aliphatic compounds.

Dehydrohalogenation is a dehalogenation/elimination reaction that is initiated by a strong base. The resulting products are the halide salt, water, and an elimination compound.

A novel reagent, sodium or potassium hydroxide mixed with a polyethylene glycol, is a very effective dehydrohalogenation agent. This reagent is shown to dehalogenate six organic compounds that are representative of low molecular weight compounds encountered in hazardous wastes: CCl_4, $CHCl_3$, CH_2Cl_2, $C_2H_4Br_2$, and CCl_3NO_2. Kinetics data for the reactions of this reagent with the six compounds is given to allow reactor design and calculation of destruction efficiency.

TABLE OF CONTENTS

NOTICE ii

FOREWORD iii

ABSTRACT iv

FIGURES vi

TABLES vii

ACKNOWLEDGMENTS viii

1.0 INTRODUCTION 1-1

1.1 BACKGROUND 1-1

1.2 OBJECTIVES 1-2

2.0 RESULTS AND CONCLUSIONS 2-1

2.1 GENERAL AND QUALITATIVE OBSERVATIONS 2-1

2.2 DETERMINATION OF REACTION KINETICS 2-4

2.3 REACTOR DESIGN 2-4

3.0 RECOMMENDATIONS 3-1

4.0 CHEMISTRY OF THE REACTION. 4-1

5.0 EXPERIMENTAL PROGRAM. 5-1

6.0 DETERMINATION OF REACTION KINETICS 6-1

6.1 REACTION RATE EQUATION 6-1

6.2 CALCULATION OF RATE CONSTANTS. 6-2

7.0 REACTOR DESIGN 7-1

REFERENCES

LIST OF FIGURES

		Page
Figure 2-1.	Infrared spectrum of tetraethylene glycol	2-3
Figure 2-2.	Infrared spectrum of foamy residue from chloroform experiment.	2-3
Figure 5-1.	Experimental set-up	5-2
Figure 5-2.	Liquid sample collection.	5-4
Figure 5-3.	GC run of halogenated test compounds plus internal standard	5-5
Figure 7-1.	Conceptual design of plug-flow, continuous feed dehydrohalogenation reactor.	7-2

TABLES

		Page
TABLE 2-1.	COMPOUNDS INVESTIGATED	2-2
TABLE 2-2.	REACTION RATE CONSTANTS BY TEMPERATURE	2-4
TABLE 2-3.	REPRESENTATIVE TUBULAR REACTOR LENGTHS	2-5
TABLE 3-1.	COMPARISON OF WASTE TREATMENT TECHNIQUES	3-2
TABLE 5-1.	GC/FID SPECIFICATIONS.	5-3
TABLE 6-1.	RATE CONSTANTS FOR EDB BY TEMPERATURE.	6-3
TABLE 6-2.	RATE CONSTANT DATA FOR LINEAR REGRESSION	6-4
TABLE 6-3.	ARRHENIUS EQUATION CONSTANTS AND RATE CONSTANTS FOR SELECTED HALOCARBONS.	6-5
TABLE 7-1.	VOLUME CALCULATIONS FOR EDB REACTOR (PLUG FLOW).	7-8
TABLE 7-2.	TUBULAR REACTOR LENGTHS.	7-9

ACKNOWLEDGMENTS

Charles Rogers and Alfred Kornel of the U. S. Environmental Protection Agency - Hazardous Waste Engineering Research Laboratory Cincinnati, Ohio are responsible for the concept and initial research of the process described in this report. Mr. Rogers was Technical Project Manager for this program. Radian Corporation, in Research Triangle Park, North Carolina, developed and conducted the experimental program under contract to EPA. John Harden of Radian was the Project Director, and George Ramsay was responsible for designing and conducting the laboratory experiments.

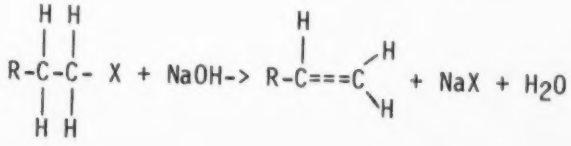
1.0 INTRODUCTION

1.1 Background

Halogenated organic compounds account for a major portion of toxic and persistent hazardous wastes. Various techniques have been proposed for destroying these constituents. Incineration is a widely used destruction technique, but has limitations.

There have been other methods proposed and used for destroying halogenated species, such as ultraviolet (UV) and UV/ozone degradation, biotreatment with specially adapted microorganisms, and sodium metal reduction. Each of these techniques has shown promise for destruction (or transformation) of the halogenated species, and each of these technologies has certain applications wherein it is the method of choice.

Preliminary work has been initiated toward development of an alternate method for the destruction of halogenated organics that is based on a classical organic chemistry technique for dehalogenation. It involves reaction of the halogenated species with ccaustic to produce an elimination reaction. The products of the reaction are the halide salts, water, and a multiple bond on the organic molecule at the site of the dehalogenation.



This reaction mechanism is referred to as dehydrohalogenation.

Typical dehydrohalogenation reactions are carried out in an initially anhydrous system in the presence of solid caustic, or a small amount of water may be used as a catalyst. These conditions lead to very vigorous, and even uncontrollable, reactions. In order to make this technology useful for the treatment of hazardous waste, three criteria must be met:

1. The reaction system must accommodate wastes containing water,
2. The reaction must be smooth and controlled, and
3. The methodology must provide treatment efficiency equivalent to or exceeding existing treatment techniques.

This report documents an experimental program initiated in HWERL[1] to validate the treatment of halogenated waste compounds by means of a novel dehydrohalogenation reagent that meets the above listed criteria. This reagent, composed of caustic mixed with a relatively small quantity of polyethylene glycol, has been shown to be effective in rapid yet controlled dehydrohalogenation in organic syntheses.[2] The polyethylene glycol acts as a catalyst in the reaction. In this program, the reagent mixture chosen for experimentation was potassium hydroxide (KOH) and tetraethylene glycol (TEG). This reagent will be referred to subsequently as KTEG.

1.2 OBJECTIVES

There were four objectives in this program:

1. Validation of the efficacy of KTEG to destroy ethylene dibromide.
2. General, qualitative observation of the reactivity of KTEG with a series of halogenated and nonhalogenated compounds to determine those showing promise for treatment with KTEG,
3. Determination of reaction kinetics data to allow design of treatment systems and calculation of treatment efficiencies, and
4. Conceptual design of a possible treatment system.

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1. Hazardous Waste Engineering Research Laboratory, Cincinnati, OH

2.0 RESULTS AND CONCLUSIONS

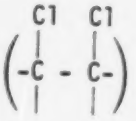
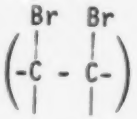
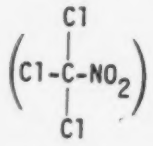
2.1 GENERAL AND QUALITATIVE OBSERVATIONS

A total of seven compounds were tested in the dehydrohalogenation system. These compounds are listed in Table 2-1 along with qualitative descriptions of the results of the dehydrohalogenation. It should be noted that several chemicals appeared to react with the tetraethylene glycol (TEG) catalyst under the reaction conditions. The mechanisms for these non-catalytic TEG reactions are not known at this time, but such reactions always resulted in an overall slowdown of the desired dehydrohalogenation. Carbon disulfide, for example, a nonhalogenated test compound, stoichiometrically reacted with the TEG to form a sticky brown sludge; this reaction prevented all further reaction of the reagent with any halogenated compounds. Carbon tetrachloride and chloropicrin both showed evidence of slight consumption of the catalyst, but this did not seriously impair their dehalogenation. The effects of such compounds in real world situations can be overcome by addition of excess reagent.

Chloroform showed an unusual reaction with the TEG. The chloroform reacted vigorously when added to the system, and it evolved a large volume of gas very quickly. If a large volume of chloroform was added to the reactor, a gray-colored foram formed, and this foam solidified into a stable open-celled spongy material. A portion of this foam was cleaned with a series of solvents and analyzed by infrared spectroscopy (IR). From this cursory analysis, the foam appeared to be a substituted form of the TEG.

Chloroform could be added in small portions to the reactor without foam formation. However, under these conditions, the chloroform reacted smoothly and consumed a small amount of the TEG in a similar manner to CCl_4 and chloropicrin.

TABLE 2-1. COMPOUNDS INVESTIGATED

CHEMICAL	RESULTS
Carbon disulfide (CS_2)	Quantitatively reacts with the TEG to form a brown sludge.
Methylene chloride (CH_2Cl_2)	Reacts slowly. Consumes some TEG.
Chloroform ($CHCl_3$)	Rapid, uncontrollable reaction if added too quickly. Forms a stable, open-celled foam. Slow addition produces a controlled reaction without foam formation. Consumes some TEG.
Carbon tetrachloride (CCl_4)	Moderate reaction rate. Consumes some TEG.
Ethylene dichloride 	Fast but controlled reaction. No evidence of reaction with TEG.
Ethylene dibromide 	Slightly faster rate than with EDC, but still controlled. No TEG consumption.
Chloropicrin 	Moderate reaction rate. Consumes some TEG.

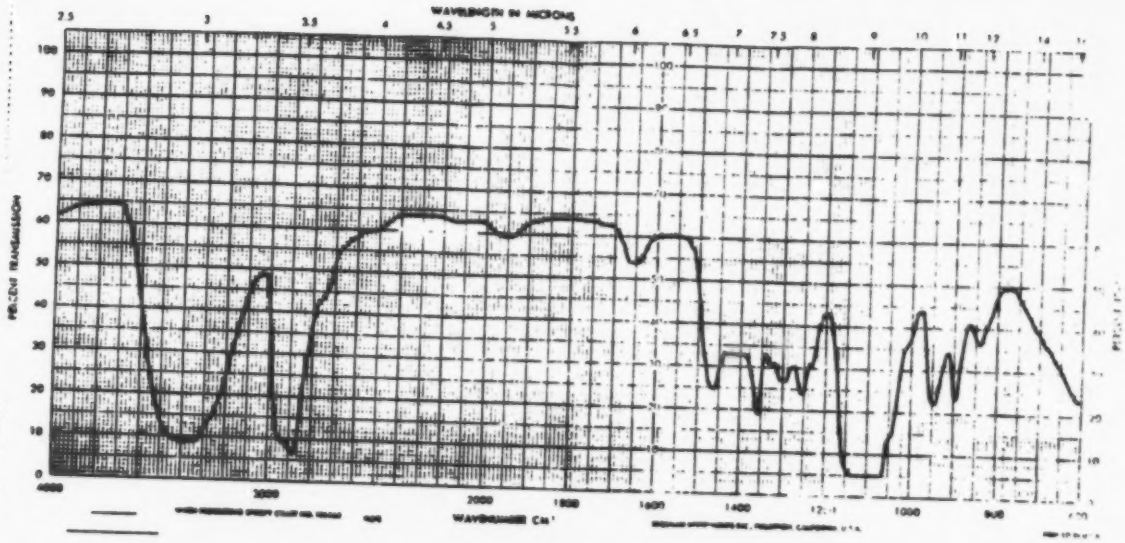


Figure 2-1 Infrared Spectrum of Tetraethylene Glycol

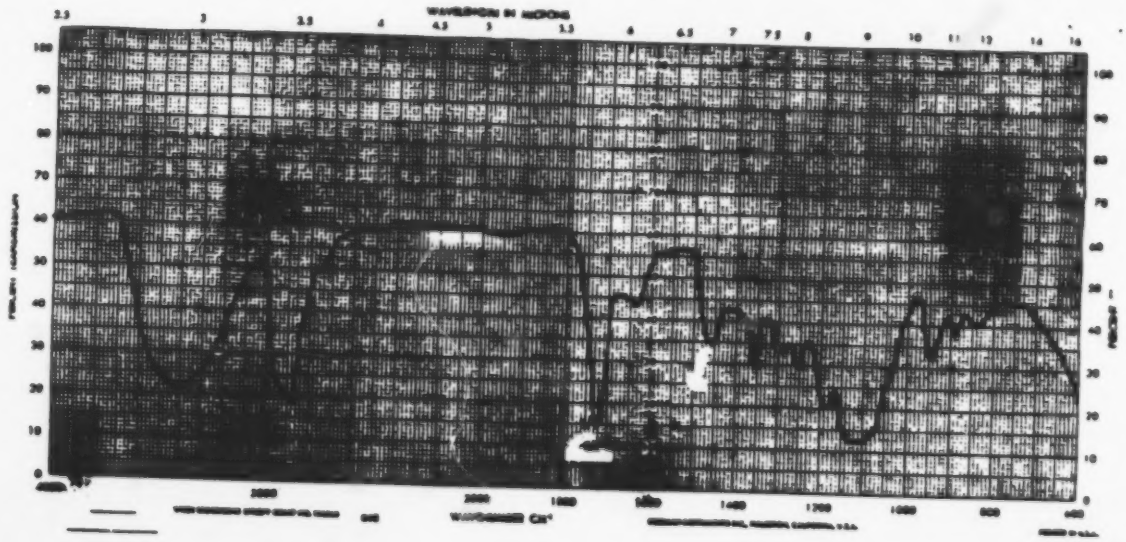


Figure 2-2 Infrared Spectrum of Foamy Residue from Chloroform Experiment

2.2 DETERMINATION OF REACTION KINETICS

The reaction rate constants for dehydrohalogenations by the KTEG reagent vary by temperature. Table 2-2 shows rate constants for six compounds over the temperature range of 21°-50°C.

TABLE 2-2. REACTION RATE CONSTANTS BY TEMPERATURE

Compound	k_a (mL Constituent/mole TEG·min)			
	21°C	30°C	40°C	50°C
Ethylene dibromide (EDB)	90.2	153	267	449
Ethylene dichloride (EDC)	102	163	265	419
Carbon tetrachloride	16.0	22.3	31.6	43.7
Chloroform	9.8	21.3	48.0	103
Methylene chloride	0.10	0.36	1.36	4.78
Chloropicrin	5.72	N/D	N/D	N/D

N/D = no data.

These rate constants may be used to design reactors and to determine the reaction efficiencies for KTEG systems. Since this particular dehydrohalogenation reaction is a first order, nonreversible reaction, the level of destruction is dependent only upon time of contact of the halogenated compound and the KTEG reagent. This means that any desired level of destruction may be accomplished by designing the reaction system for proper residence times.

The values of k_a may be easily converted to other units as needed. For example, the rate constant for EDB at 21°C on a molar basis is:

$$90.2 \frac{\text{mL EDB}}{\text{mole TEG} \cdot \text{min}} \times \frac{2.179 \text{ g EDB}}{\text{mL EDB}} \times \frac{1 \text{ mole EDB}}{187.87 \text{ g EDB}} = 1.05 \frac{\text{mole EDB}}{\text{mole TEG} \cdot \text{min}}$$

2.3 REACTOR DESIGN

Conceptual designs of reactors for treatment of halogenated wastes were developed by utilizing the kinetics data described above and the parameters listed below:

WASTE COMPOSITION	- 95% CCl_4, 5% EDB (V/V)
REACTOR TYPE	- (A) Plug flow, tubular (B) Batch
OPERATION TEMPERATURE	- 50°C
FEED RATE	- (A) 1 gal/min (B) 60 gal/hr
DESTRUCTION EFFICIENCY	- 99.999% of the EDB

Table 2-3 shows the necessary lengths for a tubular, plug-flow reactor according to the tubular inner diameter.

TABLE 2-3. REPRESENTATIVE TUBULAR REACTOR LENGTHS

Diameter (in.)	Length (ft.)
2	1,056
4	264
6	117
8	86
10	42
12	29

Alternately, a batch reactor sized to handle a feed rate of 60 gallons per hour would have a volume of 550 to 600 gallons. The batch reactor could operate at atmospheric pressure, and it could be fitted with manual or automatic valves for filling and discharging the reactor contents.

A practical design for any dehydrohalogenation waste treatment reactor must be based on realistic considerations of material costs and reactor size as well as its capability for achieving the desired treatment efficiency. The ultimate cost of treatment of a unit volume of waste is determined by adding all associated costs (system construction, operation, waste disposal, etc.), and dividing that sum by the volume of waste treated. Thus, even though operating costs of a continuous feed process are generally lower than those of a batch feed process, the high initial cost of the tubular reactor

might never be offset, if there were relatively small volumes of waste to be treated.

Modification of key design parameters, such as temperature of operation or feed rate, could change the size requirements of the tubular reactor sufficiently to make it more cost effective as a treatment system design. The design parameters of a dehydrohalogenation reactor system must be derived on a case-by-case basis for the specific wastes to be treated. This may be done by using techniques similar to those described in subsequent sections of this report.

3.0 RECOMMENDATIONS

Dehydrohalogenation technology is to be developed and evaluated as a possible alternative treatment of halocarbon wastes. In determining the relative advantages and disadvantages of this technique, it is necessary to compare it to existing treatment methods. One such comparison is made with incineration as shown in Table 3-1. This simple comparison does not provide sufficient detail for declaring one of these treatment methods superior to the other; it does, however, show that several factors must be considered in choosing one of these methods over the other. The potential advantages of dehydrohalogenation include cost, energy savings, materials recovery, and the non-production of harmful by-products. Dehydrohalogenation by-products tend to be hydrolysis products of the parent moleucle; it is highly unlikely that complex aromatic species will be produced in these reactions. The potential disadvantages of dehydrohalogenation include the production of waste gases, organics, and brine that may require disposal.

Future research with this technique should explore its practicality for treatment of contaminated soils and for scrubbing halocarbons from gaseous streams. The technique should be tested on actual wastes, such as distillation bottoms from chlorinated solvent recycle, to determine the effects of complex waste matrices on the treatment efficiency of the technique.

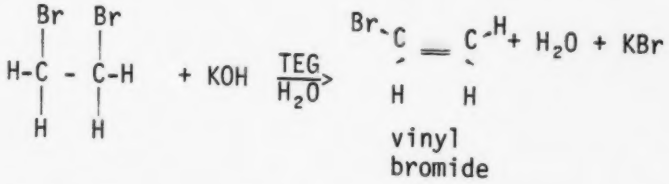
TABLE 3-1. COMPARISON OF WASTE TREATMENT TECHNIQUES

	Dehydrohalogenation	Incineration
Destruction efficiency for halocarbons	Varies with compound	Complete destruction
Relative cost for treatment	Medium	High
Residuals	Gases, organics, waste-water, inorganic salts	Gases, ash
Relative cost for residuals disposal	Unknown	Low
Temperature of treatment (Energy requirement)	Low	High

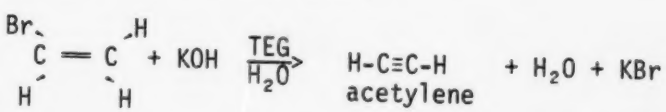
4.0 CHEMISTRY OF THE REACTION

The technique of using polyethylene glycols as catalysts in dehydrohalogenation is discussed by Kimura and Regen as an organic synthesis method.[2] Their work showed that polyethylene glycols (PEG), $(HO\text{-}(CH_2\text{-}CH_2\text{-}O)_N\text{-}H$, with N > 2) acted as phase transfer catalysts. The activities of the PEGs increased for larger values of N, up to N=5, and the reaction rate of the dehydrohalogenation system was dependent on the concentration of the PEG in the organic phase. Thus, the reaction mechanism may be considered first order or pseudo first order with respect to PEG.

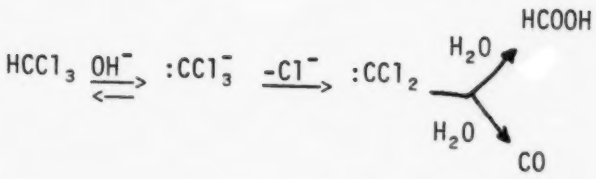
In the reaction system suggested by HWERL[1], the polyethylene glycol of choice was tetraethylene glycol (TEG) and the base chosen was potassium hydroxide (KOH). The most easily documented chemistry occurs with dihaloethanes in reaction with the KTEG reagent.[3] Ethylene dibromide (1,2-dibromoethane) illustrates this reaction:



If the vinyl bromide remains in contact with the KTEG reagent, a second dehalogenation takes place:



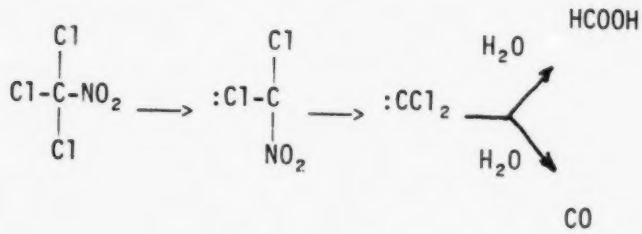
The reaction sequences for other halocarbons are not as well defined as for dihaloethanes. The effluent gases for single carbon halocarbons (e.g., carbon tetrachloride, chloroform, methylene chloride) consist primarily of carbon dioxide, but there may be other components of the gas stream. A reaction sequence for the dechlorination of chloroform using NaOH or KOH in dioxane and ethanol is documented.[4] The reaction of chloroform with the KTEG reagent may follow a similar route:



Carbon tetrachloride and methylene chloride probably react by traditional hydrolysis mechanisms:[5]

$$CCl_4 + 6\ NaOH \xrightarrow{H_2O} Na_2\ CO_3 + 4\ NaCl$$

Chloropicrin would be expected to follow a mechanism similar to chloroform:



5.0 EXPERIMENTAL PROGRAM

The experiments for both the qualitative observations and the kinetic studies were carried out in a bench scale reactor system (Figure 5-1). The reactor vessel was a 1 L three-neck flask. Attached to the flask were a thermometer, a chilled reflux condenser, a sample withdrawal system, and a mechanical stirrer. The mechanical stirrer was used instead of a magnetic stirrer because the density of the reaction mixture increased with time; if a magnetic bar were used it would become stalled in the slurry.

A typical run is outlined below: 280 g of potassium hydroxide (KOH) was dissolved in 180 mL water in the 500 mL 3-neck flask. A 5 mL portion of n-nonane was added to the flask as an internal standard. A 5 mL portion of ethylene dibromide (EDB) was added, the system was closed, and stirring was initiated. The system was observed closely for several minutes to assure that no reaction was taking place. An initial sample was taken from the reaction vessel, and then 10 mL of tetraethylene glycol (TEG) was added to the vessel.

Reaction began immediately, as evidenced by vigorous bubbling, and gas displacement versus time was plotted. Gas samples and liquid samples were taken at several intermediate reaction times and at the end of the reaction. After the gas evolution had stopped, an additional 5 mL portion of EDB was added to the reaction mixture, and the reaction resumed. The sampling and gas displacement readings were taken as before. The entire process was repeated until the mixture became too thick to stir and the reaction showed signs of slowing.

The reflux condenser was chilled to 0°C (±5°C) to prevent escape of the moderate boiling point halogenated species. Gases generated in the reaction passed through the reflux condenser and into the inverted graduated cylinder by means of a ¼" ID flexible tube. Gas samples were taken at the top of the reflux column through a septum-closed sample port by means of a gas-tight syringe.

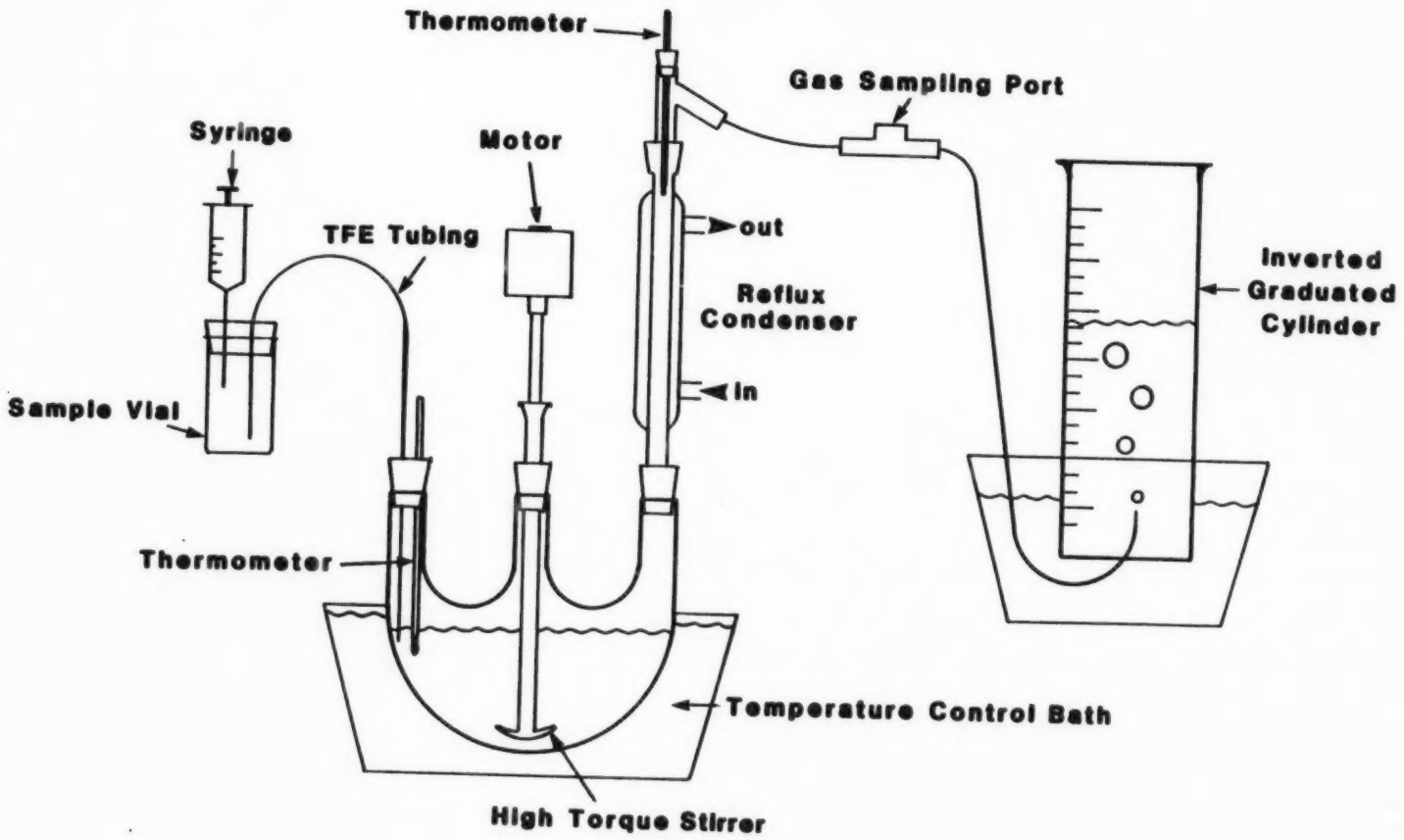


Figure 5-1. Experimental set-up.

Liquid samples were removed from the reactor through the suction mechanism shown in Figure 5-2. The empty sample vial was retained in place solely to prevent system pressure loss. Three mL of water was placed in a 5 mL sample vial and frozen. To remove a sample from the reacting mixture, the empty vial was removed and the syringe was filled with approximately ½ mL of air. Static pressure within the sample tube would usually prevent any leakage of reactor contents during the sample vial transfer. The vial containing the deionized ice was transferred to the syringe assembly, the ½ mL of air pushed through to clear the sample line, and the syringe withdrawn 1 mL to create a suction and draw sample from the reaction flask into the ice vial. The sudden cold and dilution from the melting ice halted the reaction. This facilitated a reasonable delay in actually getting the sample to analysis. The samples were then refrozen for preservation. Such samples taken at intervals during the reaction provided process "snapshots" and enabled detailed determination of the reaction kinetics.

Analyses of the gas and liquid samples were performed by GC/FID under the conditions outlined in Table 5-1.

TABLE 5-1. GC/FID SPECIFICATIONS

INSTRUMENT:	Shimadzu Mini 1
COLUMN MATERIAL:	20% SP-2100 0.1% Carbowax 1500 Supelcoport 100/120
LENGTH:	12 ft
DIAMETER:	1/8 inch
TEMPERATURE PROGRAM:	65°C/0 min, 20°C/min, 150°C final

A typical GC run showing peak resolution and relative retention times is shown in Figure 5-3.

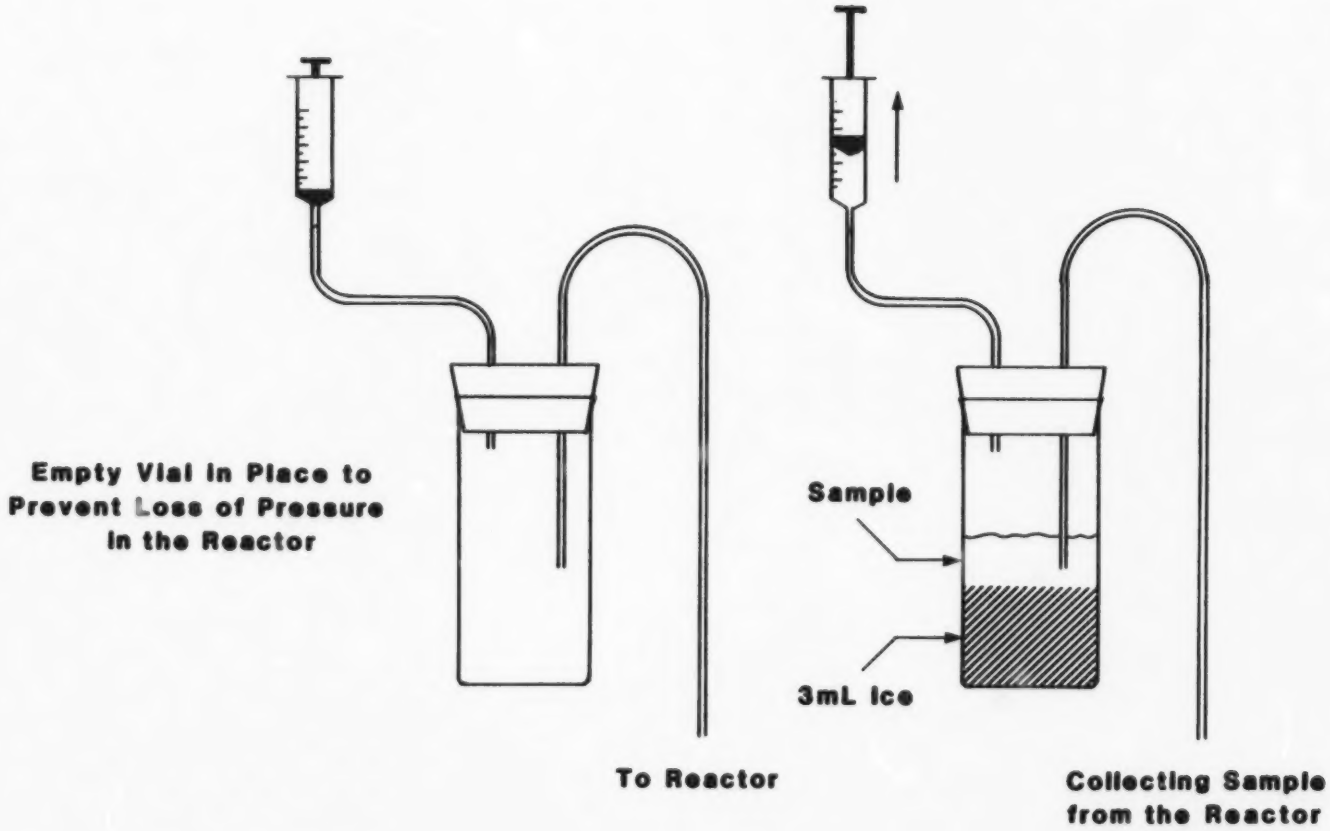


Figure 5-2. Liquid sample collection.

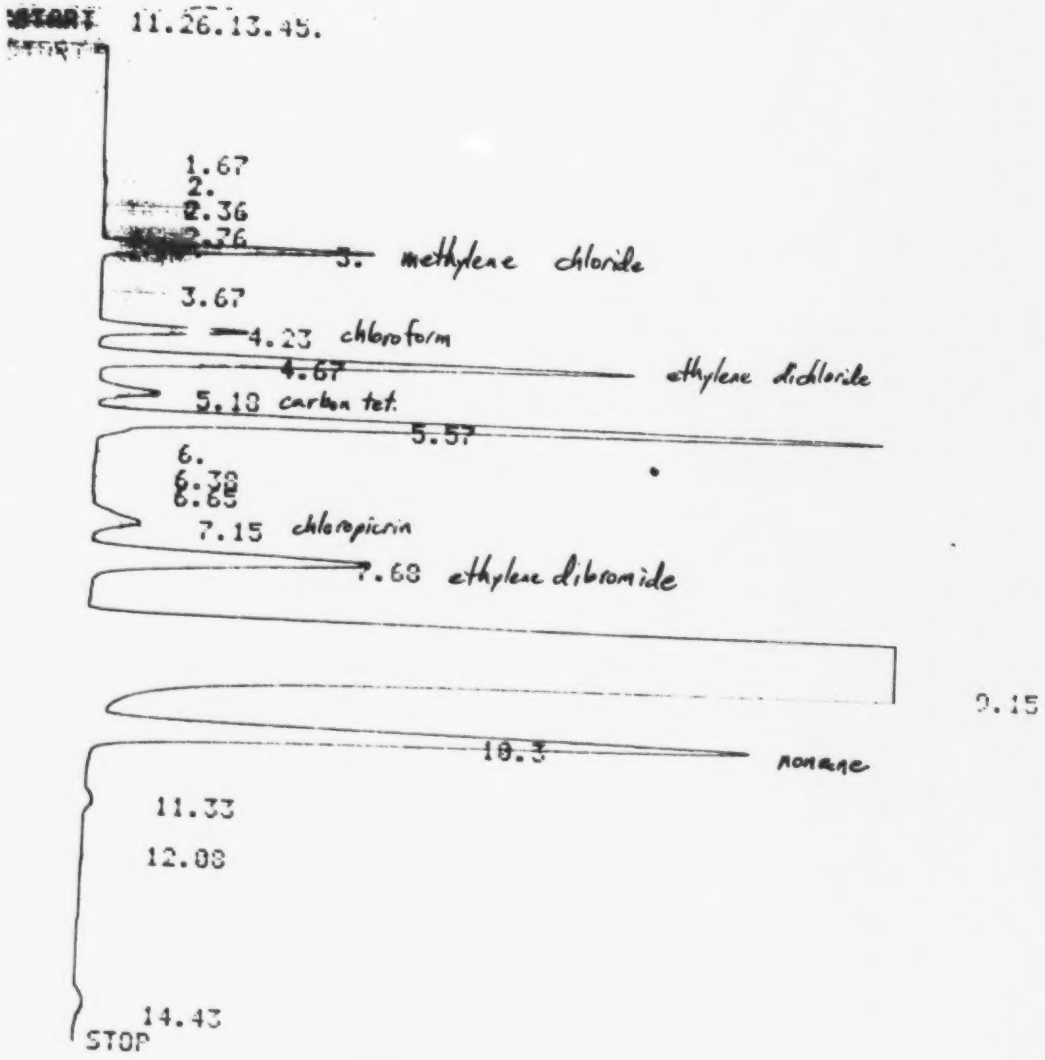


Figure 5-3. GC run of halogenated test compounds plus internal standard.

6.0 DETERMINATION OF REACTION KINETICS

6.1 REACTION RATE EQUATION

Kimura and Regen[2] determined two aspects of the dehydrohalogenation system based on polyethylene glycols (PEG). First, the reaction rate is proportional to the amount of PEG in the system, and second, no PEG is dissolved in the aqueous phase. The rate for a reaction in this system may be defined as follows:

(1) $-\frac{dN_A}{dt} = k_A C_A C_{PEG} V_o$, where

N_A = moles of constituent A.

k_A = reaction rate constant, mL of A/mole PEG · min.

(2) $\frac{-1}{V_o}\frac{dN_A}{dt} = k_A C_A C_{PEG}$

N_A = moles of constituent A.

C_A = concentration of A in the organic phase, mole/mL.

C_{PEG} = concentration of PEG in the organic phase, mole/mL.

V_o = volume of the organic phase, mL.

The fraction of A remaining at any given time may be defined as:

(3) $X_A = N_A/N_{Ai}$, where

N_{Ai} = initial moles of A in the system.

This enables further definition of several of the initial factors of the rate equation:

(4) $V_o = V_{PEG} + V_{Ai} X_A + V_M + V_P$, where

V_{Ai} = initial volume of A, mL

V_M = volume of any inert organics (e.g., nonane used as an internal standard).

V_P = volume of dehalogenation product of A, mL

N_{PEG} = moles of PEG in the system.

(5) $C_A = N_A/V_o = X_A\ N_{Ai}/V_o$

(6) $C_{PEG} = N_{PEG}/V_o$, where

Since all the organic dehalogenation products in this program are gaseous and leave the system, the term V_P becomes zero.

By substituting equations 3, 4, 5, and 6 into equation 2, we obtain:

$$(7)\quad -\frac{N_{Ai}}{V_o}\frac{dX_A}{dt} = k_A \frac{X_A N_{Ai}}{V_o}\frac{N_{PEG}}{V_o}$$

which simplifies to

$$(8)\quad -\frac{dX_A}{dt} = k_A \frac{X_A N_{PEG}}{V_o}$$

or

$$(9)\quad -\left(\frac{V_o}{X_A}\right)dX_A = k_A N_{PEG}\ dt$$

$$(10)\quad -\left(\frac{V_{PEG} + V_M + V_{Ai}X_A}{X_A}\right) dX_A = k_A N_{PEG}\ dt$$

Separation and integration yields the rate equation:

$$(11)\quad -\int_1^{X_A} \frac{V_{PEG} + V_M}{X_A}\ dX_A - \int_1^{X_A} V_{Ai}\,dX_A = \int_o^t k_A\ N_{PEG}\ dt$$

$$(12)\quad (1-X_A)V_{Ai} - (V_{PEG} + V_M)\ln X_A = k_A\ N_{PEG}\,t$$

$$(13)\quad k_A = \frac{(1-X_A)V_{Ai} - (V_{PEG} + V_M)\ln X_A}{N_{PEG}\,t}$$

6.2 CALCULATION OF RATE CONSTANTS

By substitution of experimental data into equation 13, values of k_A may be determined for various temperatures. An example calculation is presented below:

temperature = 37°C

V_{Ai} = 5 mL EDB

V_{PEG} = 10 mL PEG

V_M = 5 mL n-nonane

N_{PEG} = 0.0581 moles PEG

At t = 8 minutes, analysis of the reactor contents showed a conversion, or X_A, of 0.037.

$$k_A = \frac{(1-X_A)V_{Ai} - (V_{PEG} + V_M)\ln X_A}{N_{PEG}t}$$

$$k_A = \frac{(1-0.037)(5mL)-(10mL+5mL)\ln(0.037)}{(0.0581\ moles)(8\ minutes)}$$

k_A = 114.5 mL/mole·minute at 37°C.

Values for k_A at other temperatures were calculated in a similar manner. These are listed in Table 6-1.

TABLE 6-1. RATE CONSTANTS FOR EDB BY TEMPERATURE

k_A (mL/mole·min)	T(°C)
57.0	10
114.5	37
230.3	40
323.3	41
824.3	53

The rate constant is shown to depend on the reaction temperature. The Arrhenius equation describes this relationship between reaction rates and temperatures.

(14) $k_A = ae^{b/T}$ where a = constant
b = constant
T = temperature (K).

By taking the natural log of both sides, the equation becomes linear, and the constants a and b may be determined by linear regression:

(15) $\ln k_A = \ln a + \frac{b}{T}$

From the example in Table 6-1, we may derive Table 6-2.

TABLE 6-2. RATE CONSTANT DATA FOR LINEAR REGRESSION

k_a	$\ln k_a$	T(°C)	$\frac{1}{T}$ (K^{-1})
57.0	4.043	10	0.003534
114.5	4.741	37	0.003226
230.3	5.439	40	0.003195
323.3	5.779	41	0.003185
824.3	6.715	53	0.003067

Substituting values from Table 6-2 into a linear regression program yields the following results:

intercept = $\ln a = 22.4$, or $a = 5.28 \times 10^9$
slope = $b = -5258$
correlation factor = -0.90.

Thus, for EDB, the rate constant may be expressed as

$$k_A = 5.28 \times 10^9 \, e^{-5258/T}$$

Table 6-3 shows the factors for determining rate constants for five of the seven compounds tested. Data for the chloropicrin reaction was considered reliable only at 21°C, so a single rate constant is reported. Since carbon disulfide reacted with the catalyst, it was not considered treatable by this technique.

TABLE 6-3. ARRHENIUS EQUATION CONSTANTS AND RATE CONSTANTS FOR SELECTED HALOCARBONS

Compound	a	b	k_a (mL constituent/mole PEG·min^{-1}) 21°C	30°C	40°C	50°C
Ethylene dibromide	5.28×10^{9}	-5258	90.2	153	267	449
Ethylene dichloride	7.15×10^{8}	-4635	102	163	265	419
Carbon tetrachloride	1.16×10^{6}	-3290	16.0	22.3	31.6	43.7
Chloroform	2.29×10^{12}	-7696	9.80	21.3	48.0	103
Methylene chloride	6.00×10^{17}	-12717	0.098	0.355	1.36	4.78
Chloropicrin	----	----	5.72	---	---	---

7.0 REACTOR DESIGN

The optimum design for a reactor based on dehydrohalogenation would depend on the matrix of the waste to be treated in it and the amount of waste to be treated. For example, large volumes of easily-pumped material with a high reaction rate might be amenable to a continuous feed plug-flow reactor. Alternately, low volume wastes or wastes with high solids content and low reaction rates would be best handled in a batch reactor.

Candidate wastes for this treatment technique include fumigant formulations containing EDB that have been in storage since EPA cancelled their registration in 1983. A design exercise is presented below comparing the sizing of a plug-flow reactor to a batch reactor for treating these wastes. These example calculations illustrate the use of kinetics data generated in the experimental portions of this program and mathematical techniques from standard chemical engineering design manuals.[6,7,8] The results provide a preliminary overview of the relative sizes (and costs) of the plug-flow and batch systems.

7.1 PLUG-FLOW REACTOR

The EDB formulation wastes fall into the easily-pumped, fast reacting category. A possible treatment system for such wastes is shown in Figure 7-1. In order to evaluate the applicability of a system as shown in Figure 7-1 for treating a typical EDB waste, it is necessary to perform preliminary design calculations to determine the necessary reactor volume and dimensions. The design criteria for this reactor can be expressed in the equation:

$$(16)\quad \frac{V}{F_{Ai}} = \int_{X_{Af}}^{X_{Ai}} \frac{dX_A}{k_A C_A C_{PEG}}$$

, where V = reactor volume, mL

F_{Ai} = molar flow rate of reactant A, moles/min.

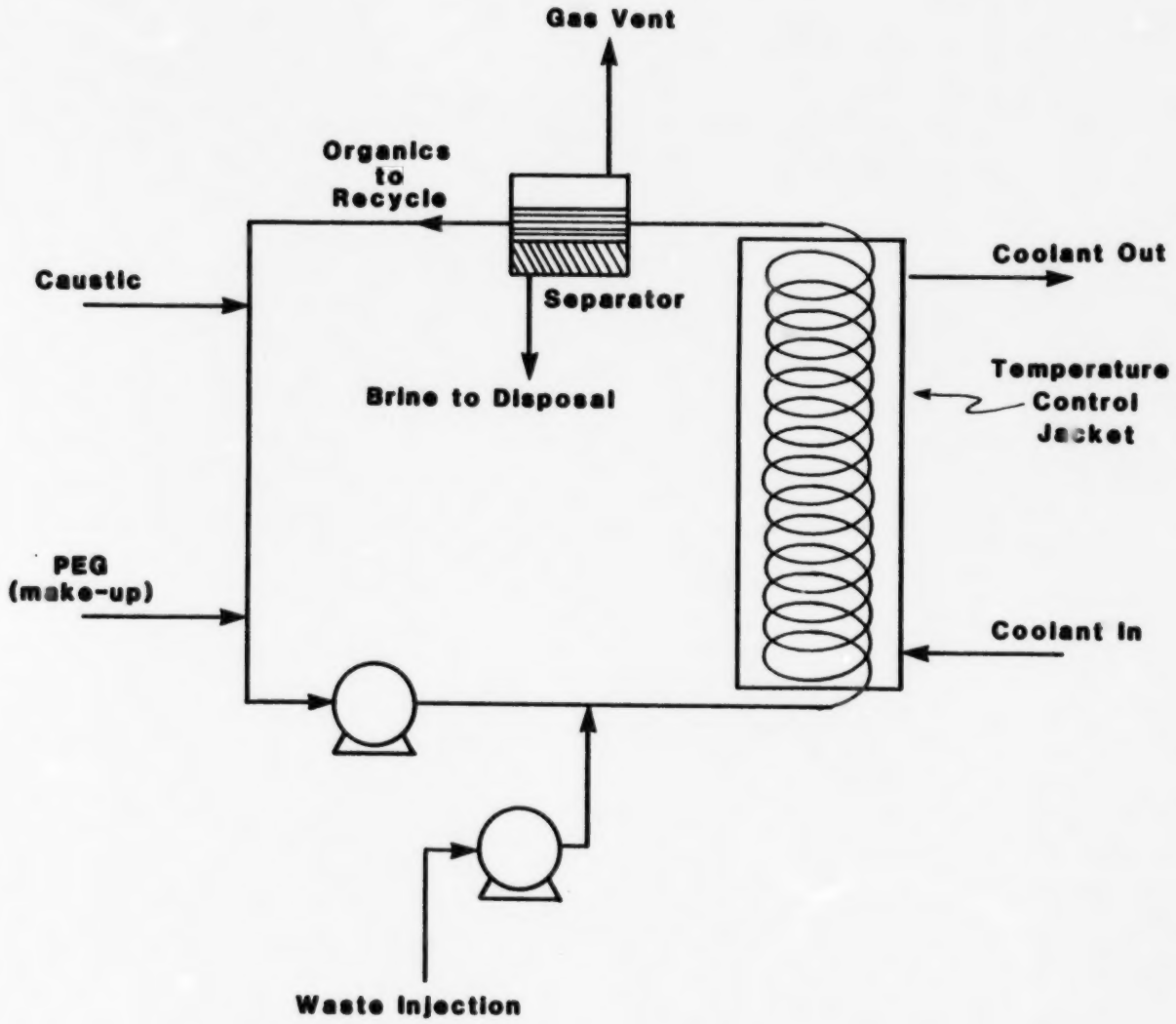


Figure 7-1. Conceptual design of plug-flow, continuous feed dehydrohalogenation reactor.

X_{Ai} = fraction of A entering a reactor segment.

X_{Af} = fraction of A leaving a reactor segment.

X_A = fraction of A remaining in the organic phase.

C_A = concentration of A in the organic phase, moles/mL.

C_{PEG} = concentration of PEG in the organic phase, moles/mL.

k_A = rate constant, mL A/mole PEG·min.

The molar concentration of A may also be expressed as:

(17) $C_A = \frac{X_A F_{Ai}}{Q_o}$ where Q_o = volumetric flowrate of the organic phase, moles/min.

Similarly, the concentration of PEG is:

(18) $C_{TEG} = F_{PEG}/Q_o$ F_{PEG} = molar flowrate of PEG, moles PEG/min.

The volumetric flowrate of the organic phase may be expressed as:

(19) $Q_o = Q_{PEG} + Q_M + Q_{Ai} X_A$, where Q_M = volumetric flowrate of inert matrix, mL/min.

Q_{Ai} = initial volumetric flowrate of A, mL/min.

Substituting (17), (18), and (19) into equation (16) gives:

$$(20)\quad \frac{V}{F_{Ai}} = \int_{X_{Af}}^{X_{Ai}} \frac{(Q_{PEG} + Q_M + Q_{Ai} X_A)^2}{k_A F_{PEG} F_{Ai} X_A} dX_A$$

which simplifies to:

$$(21)\quad \frac{Vk_A F_{PEG} F_{Ai}}{F_{Ai}} = \int_{X_{Af}}^{X_{Ai}} \frac{(Q_{PEG} + Q_M)^2}{X_A}\, dX_A + \int_{X_{Af}}^{X_{Ai}} 2Q_{Ai}\,(Q_{PEG} + Q_M)\, dX_A + \int_{X_{Af}}^{X_{Ai}} Q^2_{Ai} X_A dX_A$$

or

$$(22)\quad V = \frac{1}{k_A F_{PEG}} \left[\frac{Q^2_{Ai}}{2} (X^2_{Ai} - X^2_{Af}) + 2Q_{Ai}(Q_{PEG}+Q_M)(X_{Ai}-X_{Af}) + (Q_{PEG}+Q_M)^2 \ln \frac{X_{Ai}}{X_{Af}} \right]$$

Thus, the reactor design must be based on the following parameters:

- temperature of operation,
- rate constant of the compound to be destroyed,
- level of destruction desired, and
- flowrate.

The sizing of a reactor is best illustrated by an example. In this example, we will consider a waste made up of 95 percent CCl_4 and 5 percent EDB (V/V); the reactor will be designed on the basis of 99.999 percent destruction of the EDB. Since EDB has a much higher reaction rate than CCl_4, it will be destroyed to a far greater extent than CCl_4 in this reactor. The design approach will assume that the reactor is a series of small reactor segments, and the sizing criterion for each segment is a 10 percent loss of CCl_4 as the reacting mixture passes through it. The sizing is based on CCl_4 rather than EDB to limit the number of iterations of the calculations. The design parameters for the reactor are:

- temperature of operation - 50°C
- k_a (CCl_4, 50°C) - 43.7 mL/mole·min
- feed rate - 1 gal/min (3,785 mL/min)
- destruction efficiency (EDB) - 99.999 percent.

In the first segment, the feed of waste can be expressed as:

$$3{,}785 \frac{\text{mL waste}}{\text{min}} \times \frac{0.05 \text{ mL EDB}}{\text{mL waste}} \times \frac{2.179\text{g EDB}}{\text{mL EDB}} \times \frac{1 \text{ mole EDB}}{187.87\text{g EDB}} = 2.20 \frac{\text{moles EDB}}{\text{min}}$$

and

$$3{,}785 \frac{\text{mL waste}}{\text{min}} \times \frac{0.95 \text{ mL } CCl_4}{\text{mL waste}} \times \frac{1.594\text{g } CCl_4}{\text{mL } CCl_4} \times \frac{1 \text{ mole } CCl_4}{153.8\text{g } CCl_4} = 37.27 \text{ moles } CCl_4$$

Volumetrically, these flows are 189 $\frac{\text{mL EDB}}{\text{min}}$ and 3,596 $\frac{\text{mL } CCl_4}{\text{min}}$

The experimental data showed that the system operates best with an over-concentration of caustic. Thus, we will provide twice the stochiometric amount of NaOH required to take the CCl_4 to Na_2CO_3 and the EDB to acetylene. A concentration of 48 percent (W/W) NaOH is assumed.

$$Q_{NaOH} = \left[\left(2.20 \frac{\text{moles EDB}}{\text{min}} \times 2 \frac{\text{moles NaOH}}{\text{mole EDB}}\right) + \left(37.27 \frac{\text{moles } CCl_4}{\text{min}} \times 6 \frac{\text{moles NaOH}}{\text{mole } CCl_4}\right)\right]$$

$$\times \frac{100\text{g caustic}}{48\text{g NaOH}} \times \frac{40\text{g NaOH}}{\text{mole NaOH}} \times \frac{1 \text{ mL caustic}}{1.507\text{g caustic}} = 12{,}609 \frac{\text{mL}}{\text{min}}$$

x 2 times the stochiometric amount = 25,200 mL/min.

The polyethylene glycol of choice in this example is tetraethylene glycol (TEG). It is used at a concentration of 4.6 percent of the caustic (V/V) which was shown to be effective in the laboratory evaluations. Thus, the flowrate of TEG into the reactor may be expressed as:

$$Q_{TEG} = (.046)(25{,}200\text{mL/min}) = 1160 \frac{\text{TEG}}{\text{mL/min}}$$

On a molar basis, this becomes:

$$F_{TEG} = \left(1160 \frac{\text{mL}}{\text{min}}\right)\left(\frac{1.129\text{g}}{1 \text{ mL}}\right)\left(\frac{1 \text{ mole}}{194.23\text{g}}\right) = 6.74 \frac{\text{moles TEG}}{\text{min}}$$

Utilizing the flowrates calculated above, the volumetric ratio of EDB/CCl_4 waste to caustic to TEG is 1 to 6.66 to 0.31, respectively.

The calculations of reaction rates must be performed independently for CCl_4 and EDB. The factor Q_M, which represents the flow of inert material in the organic phase, is different depending on whether the calculations are for

EDB or CCl_4. Since the CCl_4 concentration is much higher than that of EDB from the outset, and since EDB is destroyed at a much faster rate than is CCl_4, the CCl_4 in the organic phase may be considered inert with respect to EDB. Since the concentration of CCl_4 is changing over a period of time, the flowrate in each reactor segment may be expressed as a function of concentration. In this case, with an initial flow of CCl_4 of 3596 mL/min,

$Q_M = Q_{CCl4i} X_{CCL4} = (3596 \text{ mL/min}) X_{CCl4}$

$$(23) \quad \frac{V_{TOTAL}}{V_{ORGANIC}} = \frac{Q_{TEG} + Q_M + Q_{Ai} + Q_{NaOH} + Q_{gas}}{Q_{TEG} + Q_M + Q_{Ai}}$$

The gaseous by-product flowrate may be expressed as a function of the flow of the species generating gas in the reaction:

$$(24) \quad Q_{gas} = \frac{Q_{Ai} C_A}{MW_A} (22.4 \text{ L/mole}), \text{ where } C_A = \text{density of constituent A, g/mL}$$

MW_A = molecular weight of A

In this example, most of the gas will come from the EDB reaction since most of the CO_2 generated in the CCl_4 reaction will go into solution as sodium carbonate. Thus, the gas flow may be approximately calculated as:

$$Q_{gas} = \frac{Q_{EDB}(2.179 \text{ gEDB/mL})(22.4 \text{ L/mole})(1000 \text{ mL/L})}{187.87 \text{ gEDB/mole}} = 260\, Q_{EDB}$$

The flow of CCl_4 will be considered the inert flow, Q_M.

Substituting the various flows into equation 23 gives:

$$V_{TOTAL} = \frac{(41{,}060 \text{ mL})[1160+3596+189+25{,}200+(260)(189)]}{(1160+3596+189) \text{ mL/min}} \text{ mL/min}$$

$= 658{,}330$ mL
$= 658$ L
$= 23.2$ ft^3

The total flowrate through the system for liquids and gases is 79,285 mL/min, or 2.8 ft^3/min.

Since the concentration of EDB will always be very small with respect to CCl_4, the Q_M for calculations of CCl_4 reaction rate is zero.

The factors for substitution into equation 22 are:

$\underline{CCl_4}$

Q_{Ai} = 3596 mL CCl_4/min

Q_{TEG} = 1160 mL TEG/min

Q_M = 0

k_A = 43.7 mL CCl_4/mole TEG·min

F_{TEG} = 6.39 mole/min

$\underline{EDB}$

Q_{Ai} = 189 mL EDB/min

Q_{TEG} = 1160 mL TEG/min

Q_M = 3596 $\frac{\text{mL } CCl_4}{\text{min}}$ X_{CCl4}, where X_{CCl4}= wt. fraction of CCl_4 remaining

k_A = 449 mL EDB/mole TEG·min

F_{TEG} = 6.39 mole TEG/min

By solving Equation 22 for each reactor segment, we produce the results shown in Table 7-1. This shows a total <u>organic</u> phase volume of approximately 41,000 mL. The aqueous and gas phase volumes must be added to this to derive the total reactor volume. Derivation of the total volume is presented below:

TABLE 7-1. VOLUME CALCULATIONS FOR EDB REACTOR (PLUG-FLOW)

Reactor Section	Percent of CCl_4 Remaining	Volume for Reactor Section (mL)	Percent of EDB Remaining	Percent of Reactor Used
1	90	6,270	45	15.3
2	80	5,860	19	29.5
3	70	5,470	7.1	42.9
4	60	5,090	2.3	55.3
5	50	4,750	0.69	66.8
6	40	4,470	0.15	77.7
7	30	4,280	0.022	88.1
8	20	4,330	0.0016	98.7
9	19	540	0.0010	100.0
TOTAL VOLUME		41,060 mL		

Flow in the reactor should be turbulent to insure good mixing and to avoid deposition of the precipitated inorganic salts within the reactor. The maximum pipe diameter can be approximated with a modification of the Reynolds equation:

(25) $R_e = \frac{4Q\rho}{\pi\mu d}$ where

R_e = Reynolds number, dimensionless
ρ = fluid density, g/mL
Q = flowrate, mL/sec
μ = fluid viscosity, poise (g/cm·sec)
d = pipe diameter, cm.

If we assume that the gas will separate from the fluid as it is generated, and if the inorganic salts remain at least partially in suspension, then the fluid density and viscosity will be relatively high. In the absence of actual data on these properties, the following are assumed based on observations of the laboratory system:

$$\rho = 1.5 \frac{g}{mL}$$

$$\mu = 0.013 \text{ poise}$$

The total liquid flow through the system is 30,145 mL/min, or 502 mL/sec. Thus, for turbulent flow (R_e >4000) the pipe diameter is calculated by:

$$d = \frac{4(1.5 \frac{g}{mL})(502 \frac{mL}{sec})}{\pi (0.013 \frac{g}{cm\ sec})(4000)} = 18 \text{ cm} \cong 7 \text{ in.}$$

Borderline turbulent flow (R_e=2100) would enable the use of a 14-inch diameter pipe.

The minimum diameter of the reactor would depend on pumping pressure capacities. A practical limit would probably be on the order of 2 inches. Table 7-2 shows lengths of the reactor tube as a function of tube diameter.

TABLE 7-2. TUBULAR REACTOR LENGTHS

Diameter (in)	Length (ft)
2	1,056
3	468
4	264
5	169
6	117
7	86
8	66
9	52
10	42
12	29
14	22

7.2 BATCH REACTOR

A batch reactor may be constructed of any size since the variables affecting reaction efficiency for the KTEG reagent are temperature and contact time. Once the reaction efficiency and operation temperature are

established, the contact time can be calculated. The batch reactor can then be sized to allow the desired throughput per unit time. An example batch reactor may be sized based on the CCl_4/EDB mixture described in Section 7.1. A reaction temperature of 50°C and a destruction efficiency of 99.999 percent will be used, as in the previous example.

The time of reaction is derived from a modification of equation 13:

$$t = \frac{(1-X_A)V_{Ai} - (V_{PEG}+V_M)\ln X_A}{N_{PEG}\, k_A}$$

In Section 7.1 the ratio of EDB/caustic/TEG was established as 1/6.66/0.31 by volume. Using these ratios, the k_A for EDB at 50°C, and 99.999 percent destruction efficiency gives:

$$t = \frac{(1-.00001)(0.05 \text{ mL EDB}) - (.31 \text{ mL TEG} + 0.95 \text{ mL } CCl_4)\ln 0.00001}{0.31 \text{ mL TEG} \times \frac{1.129 \text{ g TEG}}{1 \text{ mL TEG}} \times \frac{1 \text{ mole TEG}}{194.23 \text{ g TEG}} \quad 419 \frac{\text{mL EDB}}{\text{mole TEG} \cdot \text{min}}}$$

$t = 19.26$ minutes

This assumes that there is no slowdown of the EDB reaction by the concurrent CCl_4 reaction.

The holding time in the reactor is independent of the volume of the reactor. Thus, the reactor is sized according to desired throughput over a period of time. In the plug-flow reactor in Section 7.1, the throughput was established at 1 gallon per minute. A similar capacity batch reactor must be sized to accept a larger charge initially and then process that charge over a longer time period.

It is reasonable to assume a 1-hour cycle period for the batch reactor in this example: 20 minutes to charge the reactor, 20 minutes to react, and 20 minutes to discharge. Thus, the capacity of the reactor must process 60 gallons of waste per charge to equal the tubular reactor described in Section 7.1. Using the waste/caustic TEG ratios described above, the volume may be found through the following relation:

$$V = 60 \text{ gal waste} + (60 \times 6.66 \text{ g caustic}) + (60 \times .31 \text{ gal TEG})$$

$$V = 478 \text{ gal}$$

In general, vessels of less than 500 gallons are never filled to more than 85 percent of capacity.[9] For this application, then, the appropriate reactor size would be on the order of 550 to 600 gallons.

7.3 COMPARISON OF RESULTS

Because of the lengths of the tubing required for diameters of 7 inches and below, the tubular reactor would be quite large and expensive. Thus, the tubular, continuous feed plug-flow reactor is probably not the best choice for treating the waste in this example. In this case, a batch feed reactor could be constructed at a much lower initial cost. While the continuous flow reactor should provide less expensive treatment on a unit weight basis, the limited amount of waste that would be treated in the system would not compensate for the high initial cost of the reactor. Since the EDB/CCl_4 mixture is expected to be one of the most amenable wastes to this treatment technique, it is unlikely that a continuous flow tubular reactor would ever be practical for this treatment technique. Alternatively, a batch reactor would be much more flexible in its application, and its cost and treatment efficiency would enable it to be constructed to handle relatively small volumes of waste economically.

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